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Well-ordered $L1_0$ -FePt nanoparticles synthesized by improved SiO_2 -nanoreactor method

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It was found that the well-ordered $L1_0$ structure is formed in the FePt nanoparticles synthesized by the improved “ SiO_2 -nanoreactor” method, whereas the previously employed annealing condition has suffered from the presence of the unconverted fcc-FePt nanoparticles which are superparamagnetic at room temperature. The $L1_0$ -FePt nanoparticles prepared by this method showed a smooth hysteresis loop with no kink, and the room temperature coercivity reaches an extremely large value of 28 kOe, even though the particle size is 6.7 nm in diameter. The Mössbauer hyperfine parameters of the nanoparticles are very close to those of the bulk $L1_0$ -FePt alloy, indicating that they possess magnetic moments comparable to the bulk even at the particle surface. © 2007 American Institute of Physics. [DOI: 10.1063/1.2728760]

FePt alloy with the face-centered tetragonal (fct) $L1_0$ structure possesses high magnetic anisotropy energy (K_u , approximately $6 \times 10^6 \text{ J/m}^3$), which is about an order of magnitude larger than that of the currently used CoCr-based alloys.¹ This strong magnetic anisotropy can suppress superparamagnetic fluctuation of the room temperature magnetization down to a particle size of about 3 nm.² Thus, FePt nanoparticle is expected as a promising candidate for the future recording media with ultrahigh densities beyond 1 Tbit/in.²^{1,2} FePt nanoparticles synthesized by chemical solution based methods attract much attention from the viewpoint of practical use because of their well-defined morphology and easiness to handle for the fabrication of desirable arrays on a substrate through being dispersible in solvents.^{3–12} However, the chemical solution based methods can produce only disordered face-centered cubic (fcc) or partially ordered $L1_0$ -FePt nanoparticles. Post-thermal annealing at high temperatures is necessary to obtain well-crystallized $L1_0$ structure. However, coalescence and coarsening of the nanoparticles during annealing have lead to difficulties in fabricating desirable arrays on a substrate. Another problem associated with the annealing is the difficulty in controlling the direction of the magnetic easy axis.

Recently, we have solved these problems by developing a synthetic strategy named “ SiO_2 -nanoreactor” method.^{13–17} This synthetic strategy is characterized by the formation of SiO_2 layer on surface of the precursory fcc-FePt nanoparticles that suppresses the sintering of nanoparticles during annealing to form the $L1_0$ structure. Powder x-ray diffraction (XRD) and superconducting quantum interference device magnetometry studies revealed that the $L1_0$ -FePt nanoparticles synthesized by this method possess well-crystallized $L1_0$ structure and a room temperature coercivity of 18.5 kOe, even though the size is only 6.5 nm in diameter. It was also demonstrated that they can be made dispersible in various solvents with the aid of proper surfactants and that the direction of the magnetic easy axis of the solvent-dispersed nanoparticles can be controlled by an external magnetic field.^{13–15} However, it was found that the samples included a minor magnetically soft phase which behaves superparamagnetic at room temperature. This soft magnetic phase was attributed to

the fcc-FePt nanoparticles, which still remained unconverted to the $L1_0$ structure even after annealing at 900 °C for 1 h.¹⁶ For the practical applications such as magnetic recording media, it is highly desired that all nanoparticles possess the well-ordered $L1_0$ structure. Our preliminary studies revealed that longer annealing, more than 1 h at 900 °C, decreases the amount of the unconverted fcc-FePt nanoparticles without inducing the sintering of the nanoparticles.¹⁷

In this letter we report the result of characterization of the FePt nanoparticles synthesized by the improved SiO_2 -nanoreactor method. The hysteresis loop of the sample indicates no existence of the magnetically soft phase, and the coercivity reaches as large as 28 kOe at 300 K. The Mössbauer spectroscopy, which is a sensitive tool for the investigation of the local electronic state of the Fe atom, revealed that all nanoparticles prepared by this method have well-defined $L1_0$ structure comparable to the bulk $L1_0$ -FePt alloy not only at the core but also at the surface in spite of their small size.

The $L1_0$ -FePt nanoparticles were prepared based on the SiO_2 -nanoreactor method.^{13–15} In brief, fcc-FePt nanoparticles with an average particle size of 6.5 nm were prepared first according to the method of Sun *et al.*⁴ The elemental composition of the particles was determined to be $\text{Fe}_{56}\text{Pt}_{44}$ by using an atomic absorption spectrometer (Shimadzu AA-6300). The fcc-FePt nanoparticles were subsequently coated with SiO_2 layer and were annealed at 900 °C for 6 h in flowing H_2 (5%)/Ar (95%) gas to convert them to the $L1_0$ structure. We also prepared a sample annealed at 900 °C for 1 h for comparison, which has been the condition employed in the previous works.

Figure 1 shows a transmission electron microscopy (TEM) image of the nanoparticles after annealing for 6 h (JEOL, JEM-1010D). This figure clearly shows that nanoparticles were well isolated due to the SiO_2 coating. The average diameter was estimated to be 6.7 nm, which is almost the same as that of the nanoparticles annealed for 1 h, and that of the precursory fcc-FePt nanoparticles. Figure 2 shows XRD profile of the SiO_2 -coated FePt nanoparticles after annealing for 6 h using Cu $K\alpha$ radiation ($\lambda=0.154 \text{ nm}$; Rigaku, RINT2500). The XRD profile shows the superlattice reflections (001), (110), and (002), which verify the formation of ordered $L1_0$ structure. The broad peak around $2\theta=22^\circ$ comes

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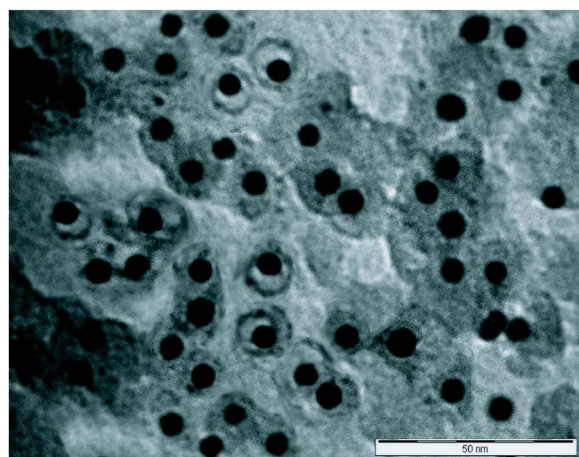


FIG. 1. TEM image of the SiO₂-coated FePt nanoparticles after annealing for 6 h.

from the amorphous SiO₂ shell. The degree of Fe/Pt ordering parameter (s) of the sample annealed for 6 h was estimated to be 0.88 by using the following equation:¹⁸

$$s^2 = \frac{\{I_{(110)}/I_{(111)}\}_{\text{measured}}}{\{I_{(110)}/I_{(111)}\}_{s=1}}. \quad (1)$$

Here $I_{(hkl)}$ is the integrated intensity of the (hkl) reflection peak. The average crystallite size (d) of the sample was estimated to be about 6.9 nm from full width at half maximum of the (111) peak by using the Scherrer formula. Results from TEM and XRD studies indicate that the nanoparticles annealed for 6 h are still well isolated and have a slightly improved Fe/Pt ordering.^{15,16}

Figure 3 shows the hysteresis loops of the samples measured at 300 K by using a physical property measurement system (Quantum Design) with an alternating current magnetization measurement system accessory. Here, M_s represents the overall sample magnetization at 90 kOe. Since the amount of SiO₂ could not be determined precisely, it was impossible to make the magnetization specific with respect to the amount of the cores. The hysteresis loop of the sample annealed for 1 h shows a kink at low magnetic field, although the coercivity reaches a large value of 20 kOe at 300 K. This kink comes from magnetically soft phases mixed in the well-ordered $L1_0$ phase.¹⁶ The amount of the magnetically soft phase at 300 K, which is estimated from

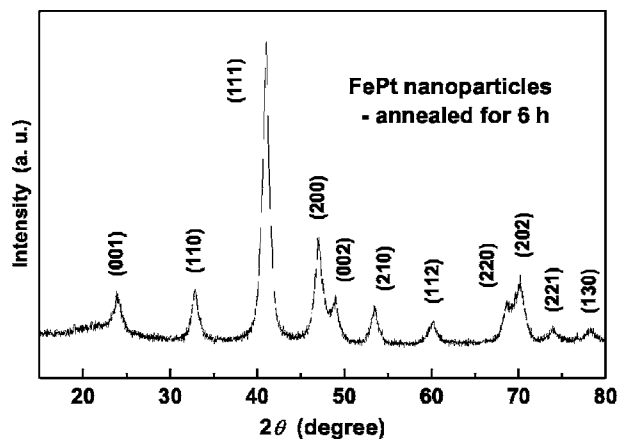


FIG. 2. XRD profile of the SiO₂-coated FePt nanoparticles after annealing for 6 h.

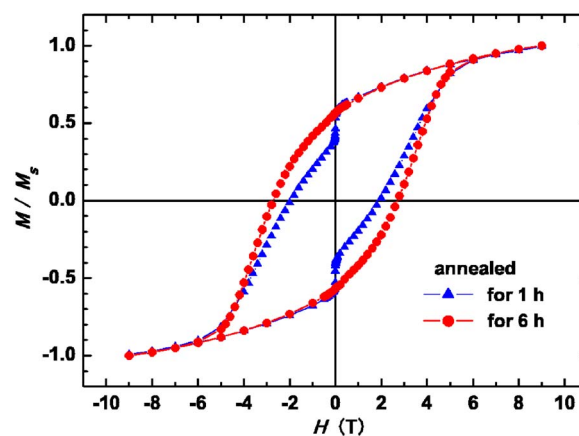


FIG. 3. (Color online) Hysteresis loops of the SiO₂-coated FePt nanoparticles after annealing for 1 and 6 h measured at 300 K.

the decrease of magnetization at the kink, is about 14%. In comparison with the sample annealed for 1 h, the hysteresis loop of the sample annealed for 6 h shows a smooth curve with no kink at low magnetic field. This indicates that annealing for 6 h can decrease the amount of the magnetically soft phases down to undetectable level by macroscopic magnetization measurement. The coercivity reaches as large as 28 kOe at 300 K.

To discuss microscopic properties of the samples, the ⁵⁷Fe Mössbauer measurements were performed at 300 K in transmission geometry using a radioactive source of ⁵⁷Co in Rh matrix with a constant acceleration technique. The Mössbauer spectra of the SiO₂-coated FePt nanoparticles after annealing for 1 and 6 h are shown in Fig. 4. The velocity scale

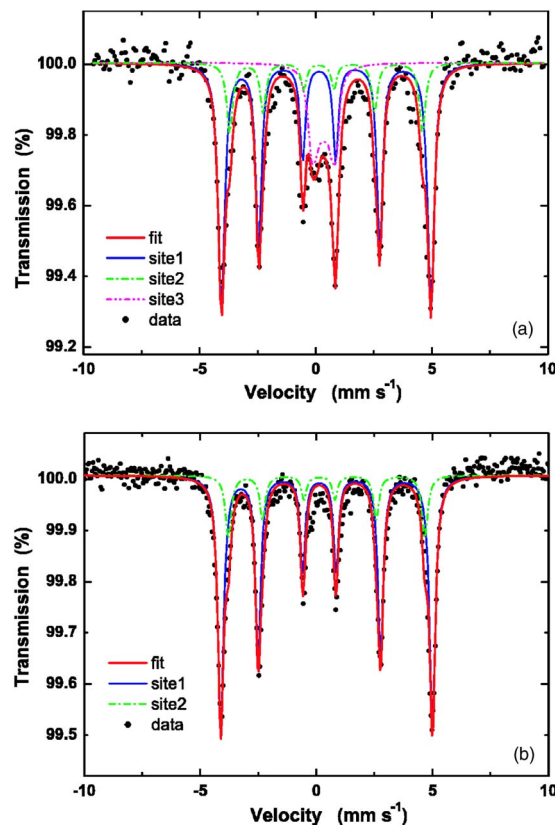


FIG. 4. (Color online) (a) Mössbauer spectrum of the SiO₂-coated FePt nanoparticles after annealing for 1 h measured at 300 K. (b) Mössbauer spectrum of the SiO₂-coated FePt nanoparticles after annealing for 6 h measured at 300 K.

TABLE I. Mössbauer hyperfine values at 300 K of the SiO₂-coated FePt nanoparticles after annealing for 1 h. The values of isomer shift (IS) are relative to α -Fe at room temperature, not corrected for the second-order Doppler shift.

	IS (mm/s)	HF (T)	QS (mm/s)	FWHM (mm/s)	AREA (%)
site 1	0.30	27.9	0.30	0.32	67.1
site 2	0.29	25.7	0.31	0.32	15.7
site 3	0.35	0	0.87	0.65	17.2

of the spectrum is relative to α -Fe at room temperature. The values of isomer shift (IS), hyperfine field (HF), quadrupole splitting (QS), full width at half maximum (FWHM), and area fraction (AREA) of each subspectrum were determined by the least squares fit. The line widths of sites 1 and 2 in both figures were assumed to be equal. This value was comparable to the linewidth of the α -Fe reference, which was equal to 0.31 mm/s.

The Mössbauer spectrum of the sample annealed for 1 h can be well fitted with three subspectra, as shown in Fig. 4(a): core- $L1_0$ -FePt (site 1), surface- $L1_0$ -FePt (site 2), and unconverted fcc nanoparticles (site 3). The parameters of the subspectra are listed in Table I. The values of the isomer shift IS and the electric quadrupole interaction QS of sites 1 and 2 are in good agreement with those of the bulk $L1_0$ -FePt reported by Goto *et al.*¹⁹ and Goto and Utsugi.²⁰ The hyperfine parameters for site 3 are fixed to values determined from the independently measured spectrum for the fcc nanoparticles which shows superparamagnetic behavior at room temperature. The fitting revealed that about 83% of the sample consists of the $L1_0$ -FePt (sites 1 and 2). It is also worth noting that the fraction of site 3 (approximately 17.2%) is in good agreement with the amount of magnetically soft phase estimated from the magnetization measurement at 300 K (approximately 14%). From the areal ratio of site 1 to site 2, about 20% of Fe atoms in the $L1_0$ -FePt nanoparticle are considered to locate at the surface. This is a reasonable value for the nanoparticle with a diameter of about 7 nm, and consistent with the TEM and XRD results.

The Mössbauer spectrum of the sample annealed for 6 h, on the other hand, consists of only two sharp sextets, as shown in Fig. 4(b). The spectrum strongly indicates the formation of well-ordered $L1_0$ phase with less fluctuation in composition as well as in crystalline structure. There is no signature of iron oxides and magnetically soft phases, and the spectrum thus can be well fitted with only two subspectra: core- $L1_0$ -FePt (site 1) and surface- $L1_0$ -FePt (site 2). The site parameters are listed in Table II. The values of the isomer shift IS and the electric quadrupole interaction QS of each site are very close to those of the bulk $L1_0$ -FePt at room temperature. It should be noted that the hyperfine field of site 2 is close to the bulk value, indicating that the magnetic moment is comparable to that of the bulk alloy even at the surface of the nanoparticle. These results strongly indicate that the nanoparticles possess well-ordered $L1_0$ structure. From the areal ratio of site 1 to site 2, the amount of the Fe atoms located at the surface is again estimated to be about 20%, which is consistent with the average diameter of about 7 nm determined by the TEM and XRD measurements.

In conclusion, the $L1_0$ -FePt nanoparticles without magnetically soft inclusion can be synthesized by the improved

TABLE II. Mössbauer hyperfine values at 300 K of the SiO₂-coated FePt nanoparticles after annealing for 6 h. The values of isomer shift (IS) are relative to α -Fe at room temperature, not corrected for the second-order Doppler shift.

	IS (mm/s)	HF (T)	QS (mm/s)	FWHM (mm/s)	AREA (%)
site 1	0.30	28.1	0.30	0.32	80.1
site 2	0.29	26.2	0.31	0.32	19.9

SiO₂-nanoreactor method. The TEM, XRD, magnetization, and Mössbauer studies unambiguously showed that the well-ordered $L1_0$ structure is formed in the nanoparticles. The $L1_0$ -FePt nanoparticles showed a smooth hysteresis loop with no kink, and the room temperature coercivity reaches an extremely large value of 28 kOe, in spite of the very small particle size of 6.7 nm in diameter. Microscopic characterization by the Mössbauer spectroscopy proved that the $L1_0$ -FePt nanoparticles synthesized by this method have magnetic moments comparable to that of the bulk state even at the particle surface. With the advantage of being dispersible in various solvents, they are a promising material for the realization of future ultrahigh density recording media.

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